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## **LIQUID PHASE DEPOSITION OF ELECTROCHROMIC THIN FILMS**

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## Abstract

Thin films of titanium, zirconium and nickel oxides were deposited on conductive SnO<sub>2</sub>:F glass substrates by immersion in aqueous solutions. The films are transparent, conformal, of uniform thickness and appearance, and adhere strongly to the substrates. On electrochemical cycling, TiO<sub>2</sub>, mixed TiO<sub>2</sub>-ZrO<sub>2</sub>, and NiO<sub>x</sub> films exhibited stable electrochromism with high coloration efficiencies. These nickel oxide films were particularly stable compared with films prepared by other non-vacuum techniques. The method is simple, inexpensive, energy efficient, and readily scalable to larger substrates.

## Introduction

Liquid phase deposition (LPD, also known as chemical bath deposition) of oxide films was first realized by Nagayama et al. [1], who used the technique to prepare SiO<sub>2</sub> coatings on silicon wafers. The process has since been extended to formation of other oxides, including those of Ti, Sn, Zr, V, Fe, Ni, Zn and Cd [2-9]. The method involves immersion of a substrate in an aqueous solution containing a precursor species (commonly a fluoro-anion) which hydrolyzes slowly to produce a supersaturated solution of the desired oxide, which then precipitates preferentially on the substrate surface, producing a conformal coating. LPD SiO<sub>2</sub> has received considerable attention in the semiconductor industry, and many modifications of the deposition conditions have been explored to optimize the electronic properties, which are affected by the crystallinity and by residual fluoride or hydroxide content. Among the transition metal oxides, LPD of TiO<sub>2</sub>, pioneered by Deki and co-workers, has been studied most extensively [10-17]. While these films have been prepared for a wide range of purposes, they do not appear to have been used as electrochromic coatings. Here we present details of the LPD preparation and characterization of electrochromic titanium oxide, mixed titanium/zirconium oxide, and nickel oxide thin films.

## Experimental

Clean SnO<sub>2</sub>:F glass substrates, masked with polyimide tape to prevent deposition on the non-conductive sides, were used for all the films deposited in this work. LPD titanium dioxide films were prepared following the method given in Ref. 13. The substrates, placed vertically in a freshly prepared solution containing 0.1 M (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> and 0.2 M H<sub>3</sub>BO<sub>3</sub>, were kept at 30°C for 16 to 72 h. They were then removed and washed with deionized water. After removing the tape masks, the coated substrates were dried at 75°C. Zirconium dioxide films were deposited in the same manner from 0.1 M (NH<sub>4</sub>)<sub>2</sub>ZrF<sub>6</sub> and 0.2 M H<sub>3</sub>BO<sub>3</sub>. Electrochemical cycling of these films was carried out at a scan rate of 2 mV/s in a 50 mL fused silica cuvette containing 1 M LiClO<sub>4</sub> electrolyte, using lithium foil counter and reference electrodes. Photopic transmittance was

monitored by an International Light silicon detector with output coupled to the computerized potentiostat/galvanostat (Arbin, Inc.).

LPD nickel oxide films were prepared according to the method of Ref. 4. A saturated solution of  $\text{NiF}_2$  was prepared by stirring excess  $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$  in deionized water overnight, followed by filtration to remove suspended solids. The deposition solution was made up by mixing 10 mL of saturated  $\text{NiF}_2$  with 20 mL of 0.5 M  $\text{H}_3\text{BO}_3$ . Substrates were immersed for 16 h at  $30^\circ\text{C}$ , then removed and rinsed with deionized water. Chemically deposited  $\text{Ni}(\text{OH})_2$  films were prepared by alternately dipping substrates in 1 M NaOH and 0.01 M  $\text{NiSO}_4$  solutions until a fairly uniform, but poorly adherent coating was obtained. Electrochemical cycling of  $\text{NiO}_x$  films was carried out at 2 mV/s in 0.1 M NaOH electrolyte, using a platinum foil counter electrode and an HgO/Hg reference electrode (Radiometer). Grazing angle X-ray diffraction patterns were obtained using a Siemens thin film diffractometer with an incident beam angle of  $0.5^\circ$  from the sample surface.

## Results and Discussion

Titanium dioxide films deposited after 16 h were 110 nm thick, clear, uniform, and transparent. Longer deposition times yielded somewhat thicker films, but these were not as clear. Under an optical microscope, small crystallites could be seen on the surface of the thicker films. XRD patterns from the films as-deposited showed only reflections due to the underlying  $\text{SnO}_2\text{:F}$  layer. On heating to  $200^\circ\text{C}$  for 1 h, very weak peaks attributable to anatase  $\text{TiO}_2$  were observed. Following heating to  $400^\circ\text{C}$ , rutile  $\text{TiO}_2$  peaks dominated the pattern. Despite their poor crystallinity, the unannealed films exhibited excellent electrochromic response and stability on cycling in lithium electrolyte. Figure 1 shows the 336<sup>th</sup> cycle for a 110 nm LPD  $\text{TiO}_2$  film, deposited over a 16 h period. The coloration efficiency was  $36 \text{ cm}^2/\text{C}$ , and was constant over the full transmittance range. The XRD pattern from this sample after cycling was identical to the uncycled sample. Heat-treated films had similar coloration ranges, but lower maximum transmittance.

The remarkable ability of LPD films to conform to irregular surfaces is illustrated in Figure 2, an optical micrograph of an LPD  $\text{TiO}_2$  film deposited over a thermally fractured sol-gel tungsten oxide film. The LPD coating spans 10 to 15  $\mu\text{m}$  gaps in the 400 nm-thick underlying layer. After annealing at  $200^\circ\text{C}$ , this coating was still intact. The small holes in the LPD film were caused by bubbles on the substrate surface. These can be eliminated by very brief (1-5 s) ultrasonic treatment. The deposition process can be accelerated by more intense ultrasonic treatment. A deposition bath containing substrates and fresh solution were placed in an ultrasonic cleaning bath for 5 m, then removed and allowed to sit undisturbed. A temperature rise of about  $5^\circ$  was induced by the ultrasonic treatment. A clear, 100 nm  $\text{TiO}_2$  film was deposited after 1 h. Longer times led to non-uniform deposition. Cyclic voltammetry (cycle 119) for this sample is shown in Figure 3. The narrower peaks suggest somewhat greater crystallinity in this sample. The smaller optical range and lower coloration efficiency ( $26 \text{ cm}^2/\text{C}$ ) could be due to non-uniform deposition. Longer exposures to ultrasound produced films very rapidly, but they were of poor visual quality and displayed patterns suggesting varying energy input at different places on the substrate.

Zirconium oxide was deposited in the same manner as  $\text{TiO}_2$ . These were also transparent and strongly adherent. The deposition rate was somewhat slower, as 24 h were required to obtain a

100 nm film at 25°C. These samples had low lithium insertion capacities and showed no electrochromism. Co-deposition of TiO<sub>2</sub> and ZrO<sub>2</sub> was accomplished by mixing the metal precursor solutions (Ti:Zr = 2:1) before adding H<sub>3</sub>BO<sub>3</sub>. The 90 nm mixed oxide film deposited in 16 h was again clear and adherent. Its electrochromic behavior (Fig. 4) was different from that of pure TiO<sub>2</sub> samples. The electrochromic response was, as expected, lower (26 cm<sup>2</sup>/C), and was limited to a narrower voltage range. The cathodic peak is shifted up by about 0.15 V, indicating improved electrochemical reversibility.

Successful liquid phase deposition of nickel oxide films required the use of freshly prepared NiF<sub>2</sub> solutions and precise temperature control. Day-old NiF<sub>2</sub> solutions did not yield films of measurable thickness, probably due to hydrolysis. On removal from the bath, the coatings (50-75 nm) were pale brown in color. After drying at 75°C for 1 h, they were nearly transparent. Due to uneven film boundaries, we were unable to measure the film thicknesses accurately. As-deposited NiO<sub>x</sub> films were also amorphous. After heating at 200°C in air for 1 h, a weak reflection attributable to cubic NiO was detected. On further heating at 400°C for 2 h, this peak was stronger, but the underlying SnO<sub>2</sub> still dominated the pattern. A sharp anodic peak at 0.45 V (Fig. 5) produced an equally abrupt decrease in transmittance. The cathodic peak at 0.32 V is broader, and the bleaching response slower. This behavior contrasts strongly with that of a chemically deposited Ni(OH)<sub>2</sub> film (Fig. 6). Here, the response is sluggish. There is no well-defined anodic peak, and the cathodic peak is shifted to -0.2 V. The wider voltage range is necessary to achieve complete switching. The transparent state is also relatively poor, probably due to scattering from the uneven surface. While the coloration efficiency of both types of nickel oxide films is quite high (ca. 70 cm<sup>2</sup>/C), the LPD film is more stable (Fig. 7). The chemically deposited film began to fall off the substrate after a few cycles (Fig. 8).

A mixed TiO<sub>2</sub> – NiO<sub>x</sub> film was also prepared by deposition from mixed metal precursors using an H<sub>3</sub>BO<sub>3</sub> concentration appropriate for TiO<sub>2</sub>. Because the deposition parameters for the two pure oxides are different, the mixed film is not as homogeneous as in the case of TiO<sub>2</sub> – ZrO<sub>2</sub>. Although the color of the film (faint pink) indicates the presence of nickel oxide throughout, there are also larger, segregated NiO<sub>x</sub> particles scattered through the coating (Fig. 9). This sample was prepared in hopes of producing a photochromic film [18], but it had little or no electrochemical capacity in either alkaline or lithium electrolytes, and was not photochromic.

## Conclusions

The mechanisms by which LPD films are formed are complex and vary from one chemical system to another. The fluoride approach described here is not unique, but has proved to produce high quality coatings. The parameters that can be adjusted to optimize film properties and deposition rates include concentrations, temperatures, induction times, substrate preconditioning, ultrasound or other energy inputs, bath circulation and chemistry manipulation during deposition, and post-deposition treatments. Once established, however, the process is highly reproducible.

Liquid phase deposition has been shown in this work and that of others to be a reliable and efficient method to prepare thin films of pure and mixed oxides. The range of materials studied to date includes electrodes of different types, electrolytes, and transparent electronic conductors. It should be possible, therefore, to build up complete electrochromic devices simply by sequential deposition in a series of LPD baths. The conformal nature of the coatings may allow

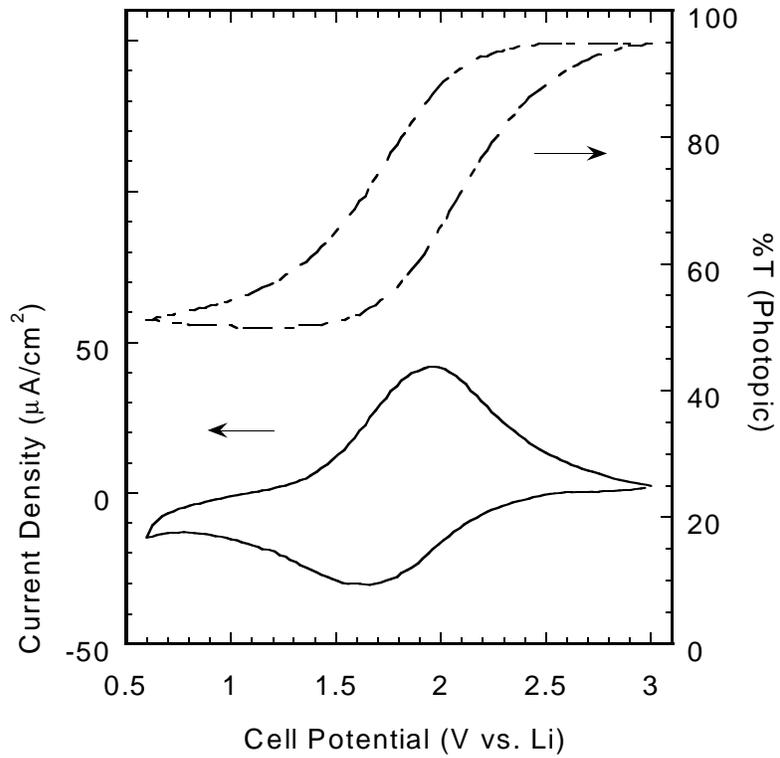
the use of a wider range of substrate shapes and sizes than are possible with current film deposition techniques.

### **Acknowledgment**

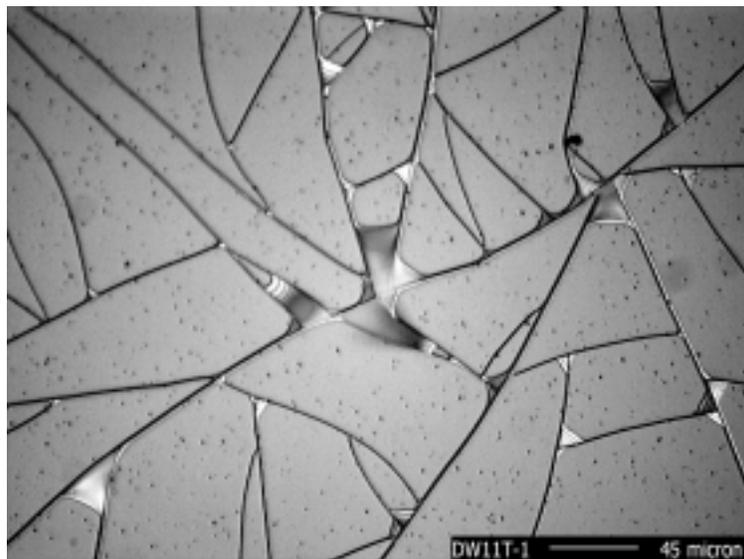
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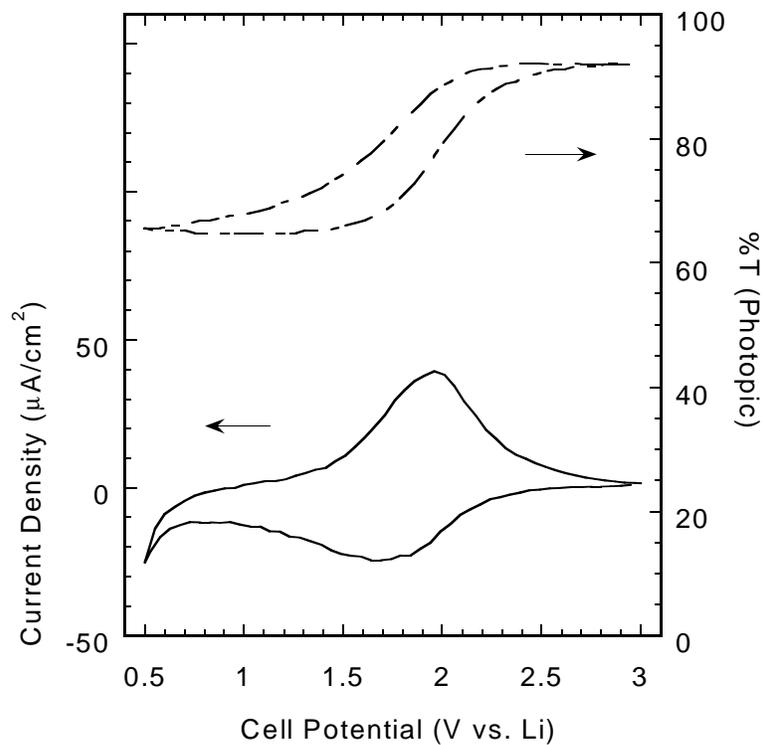
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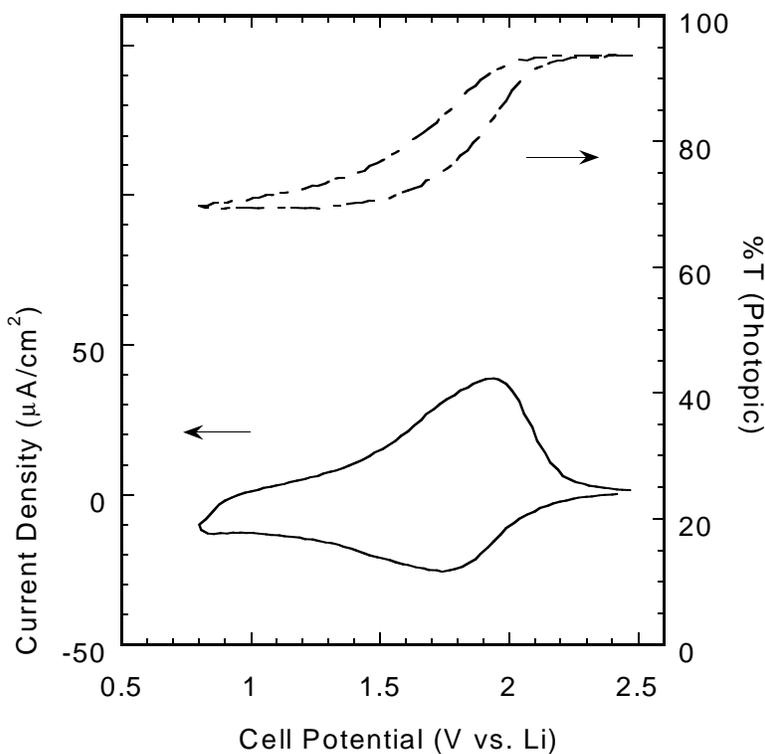
**Figure 1. Current and %T vs. potential for 110 nm LPD TiO<sub>2</sub> on SnO<sub>2</sub>:F coated glass.**



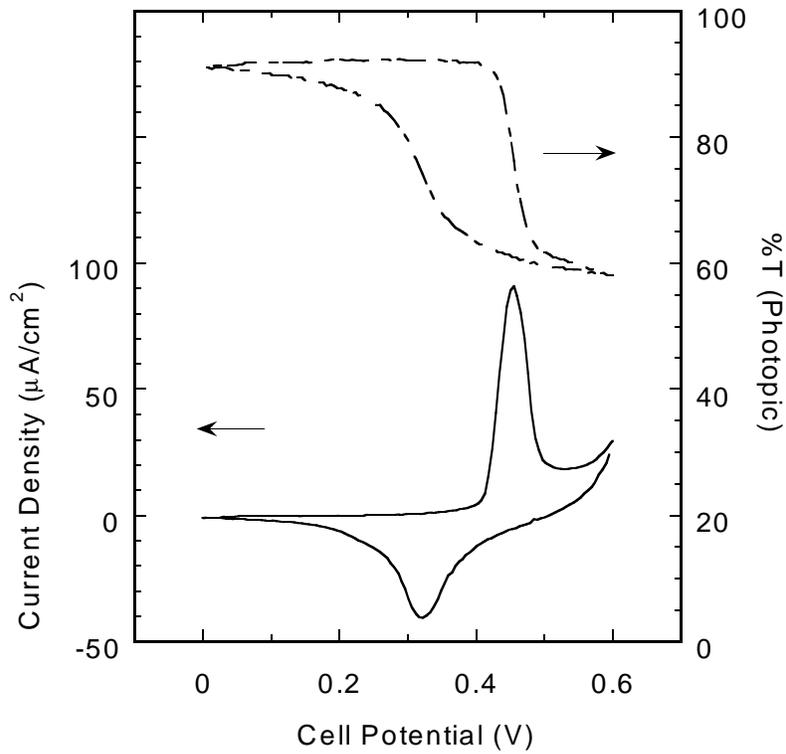
**Figure 2. Optical micrograph of LPD TiO<sub>2</sub> over sol-gel WO<sub>3</sub> (ITO substrate).**



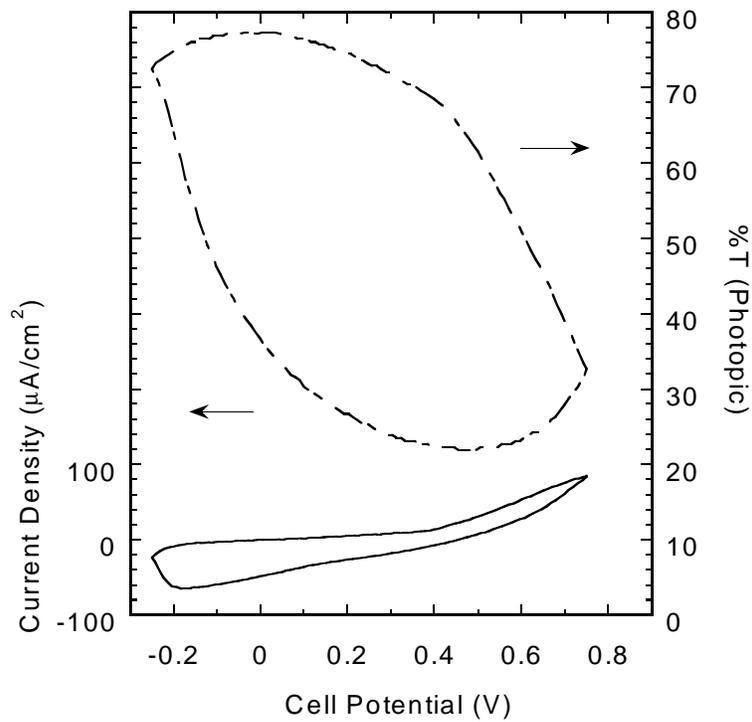
**Figure 3. Current and %T vs. potential for 100 nm LPD TiO<sub>2</sub> prepared using ultrasound.**



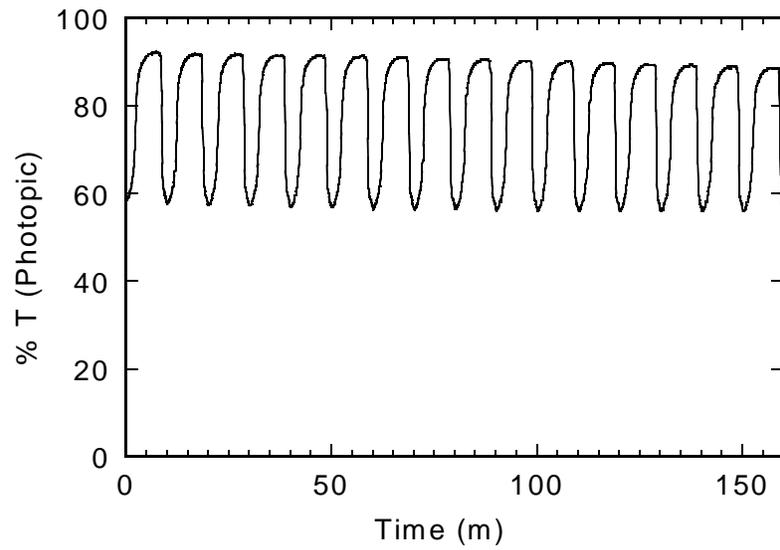
**Figure 4. Current and %T vs. potential for 90 nm LPD TiO<sub>2</sub>-ZrO<sub>2</sub> on SnO<sub>2</sub>:F coated glass.**



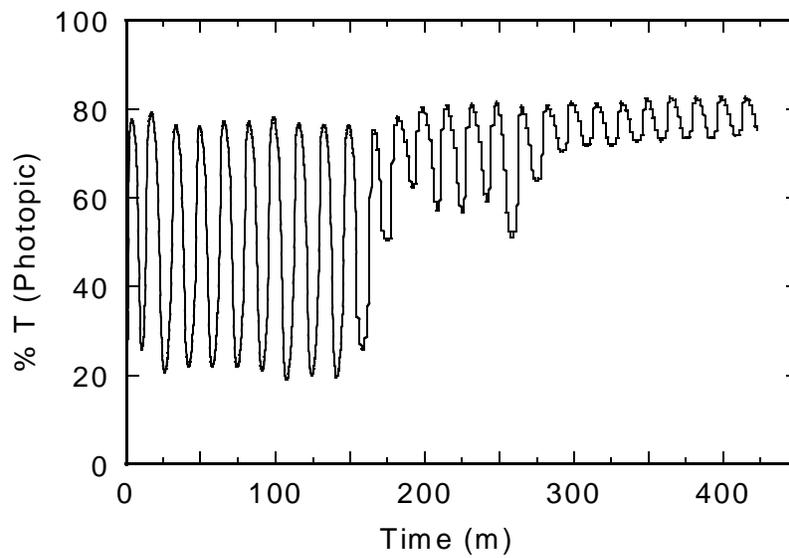
**Figure 5. Current and %T vs. potential for ca. 60 nm LPD NiO<sub>x</sub> on SnO<sub>2</sub>:F coated glass.**



**Figure 6. Current and %T vs. potential for chemically deposited Ni(OH)<sub>2</sub> on SnO<sub>2</sub>:F coated glass.**



**Figure 7. Cycling stability of LPD NiOx.**



**Figure 8. Cycling stability of chemically deposited Ni(OH)2.**

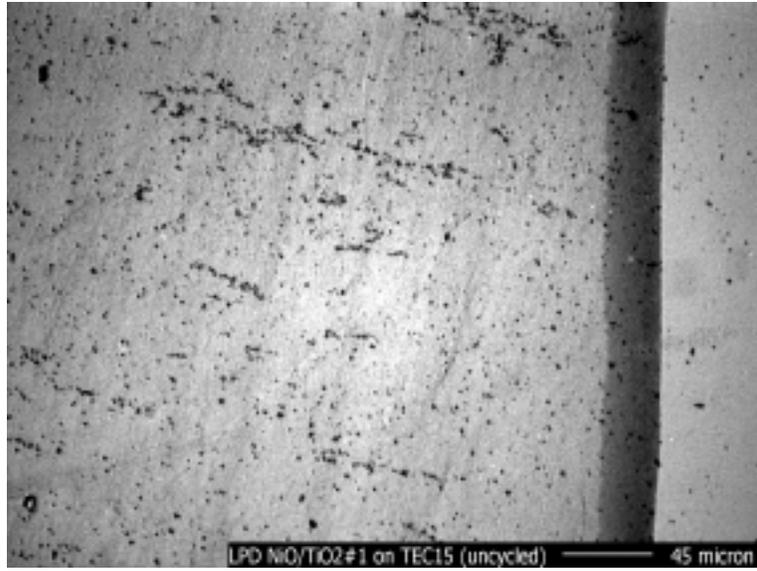


Figure 9. Optical micrograph of LPD TiO<sub>2</sub>-NiO<sub>x</sub> on SnO<sub>2</sub>:F coated glass.